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ELECTROPHILIC DISPLACEMENT REACTIONS INVOLVING ORGANOBORON COMPOUNDS

KINETICS OF REACTIONS OF AROMATIC BORONIC ACIDS WITH HYDROGEN PEROXIDE, BROMINE AND IODINE

H. G. Kuivila
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Technical Report Number 1

Office of Naval Research
Under Contract: Nonr 806(01), NR 055307

For period 1 June 1952 to 15 June 1953

Department of Chemistry
University of New Hampshire
Durham, N. H.

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The investigations described in this report were carried out under contract Nonr 806(01), NR 055307 with the exception of the work with iodine which was done without charge to the contract. The work of R. M. Williams and E. J. Soboczenski will form the basis of their M. S. theses and that of L. E. Benjamin is reported in his senior thesis, June 1953.

SUMMARY

I.

The reaction between hydrogen peroxide and benzeneboronic acid has been subjected to kinetic investigation. Above pH 3 two ionic mechanisms are distinguishable; each is first order

$$C_6H_5B(OH)_2 + H_2O_2 \rightarrow C_6H_5OH + B(OH)_3$$

in peroxide, one is first order and the other is second order in boronic acid. The rates of both reactions increase with pH, but are independent of buffer concentration and buffer constituents with the exception of citrate and tartrate which exert specific catalytic effects. In moderately strong solutions of perchloric and sulfuric acids a reaction first order in each reactant is observed. Its rate increases with acidity.

Rates of reaction of thirteen _meta_ and _para_ substituted benzeneboronic acids with hydrogen peroxide in 25% aqueous methanol 1 molar in perchloric acid have been determined. The rate constants are correlated by the Hammett equation.

On the basis of these results several conclusions concerning the mechanisms of the reaction have been drawn.

II.

The kinetics of the reaction between _p_-methoxybenzeneboronic acid and iodine have been studied in 5% aqueous

$$CH_3OC_6H_4B(OH)_2 + I_2 + H_2O \rightarrow CH_3OC_6H_4I + HI + B(OH)_3$$

methanol at 25.1°. Straightforward second order kinetics are observed. The rate is proportional to the inverse first power of both iodide ion and hydrogen ion concentrations. In acetate buffers the rate decreases with buffer concentration. This decrease appears to be due to the acetic acid.

These results demonstrate that molecular iodine attacks a p-methoxybenzeneboronate anion in the rate determining step.

III. Studies on the kinetics and mechanism of the reaction between aromatic boronic acids and bromine have been continued.

A. For investigations on the effect of substituents p-iodobenzeneboronic acid, whose preparation has not been reported in the literature, has been synthesized by the following reaction.

$$\begin{tikzcd}
p\text{-}C_6H_4I_2 + Mg \arrow[r] & p\text{-}I\ C_6H_4MgI \arrow[r, "(BuO)_3B"] & p - IC_6H_4B(OBu)_2 \arrow[dl, "H_2O"] \\
 & p - I\ C_6H_4B(OH)_2 &
\end{tikzcd}$$

Attempts to prepare m-iodobenzeneboronic acid have been unsuccessful to date. Known boronic acids with the following substituents have been prepared for this study: m - OCH_3, m - Br, m - F, p - F and p - C_6H_5.

B. Studies on the kinetics of the reaction between m-chlorobenzeneboronic acid in aqueous solution to supplement previous work in aqueous acetic acid have been initiated. Results obtained to date indicate second order kinetics and reciprocal dependence of rate on bromide ion concentration. Thus, moleculer bromine must be the brominating agent.

I. KINETICS OF THE REACTION BETWEEN HYDROGEN PEROXIDE AND BENZENEBORONIC ACID.

Among the reactions of benzeneboronic acid that with hydrogen peroxide is particularly interesting.[1] It is the only reaction involving replacement of the boronic acid function

$$C_6H_5B(OH)_2 + HOOH \rightarrow C_6H_5OH + B(OH)_3$$

which both aromatic and aliphatic[2] boronic acids are known to undergo under comparable conditions. A second point of interest involves the relative ease of replacement of hydrogen and the boronic acid function in aromatic compounds. Both are replaced with comparable ease by halogens[2,3]. Replacement of hydrogen by hydroxyl, however, is not nearly as facile as replacement of the boronic acid group. The former requires either a strongly basic medium and the presence of hydroxyl groups in the ring[4]

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(1) A. D. Ainley and F. Challenger, J. Chem. Soc. 2171 (1930)

(2) H. R. Snyder, J. A. Kuck and J. R. Johnson, J. Am. Chem. Soc., 60, 105 (1938)

(3) N. N. Melnikov, J. Gen. Chem. (U.S.S.R.) 6, 636 (1931); Chem. Abstr. 30, 5571 (1936)

(4) R. G. Jones and H. A. Shonle, J. Am. Chem. Soc., 67, 1034 (1945)

or catalysis by iron salts[5] in which case a free radical mechanism is clearly indicated.

An investigation of the kinetics of the reaction between benzeneboronic acid and hydrogen peroxide is reported herein. The results obtained to date suggest mechanisms which render the above observations reasonable.

EXPERIMENTAL

Materials. Benzeneboronic acid was prepared as described by Bean and Johnson[6] and stored as the anhydride, m.p. 214-216°[7]. Chloroacetic acid (Matheson) was recrystallized from benzene and the sodium salt prepared by addition of the acid to sodium methoxide in anhydrous methanol. All other reagents were the purest grade available commercially and were used without further purification. Sodium perchlorate was used in adjusting ionic strengths.

Stoichiometry of the Reaction. A solution at pH 5.6, 0.0500M in boronic acid and 0.64 M in hydrogen peroxide was allowed to stand three hours. From previous rate measurements this period was known to be long enough for greater than 99% consumption of

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(5) A. Chwala and M. Pailar, J. Prakt. Chem., 152, 45 (1939). H. Goldhammer, Biochem. Z., 189, 81 (1927)

(6) F. R. Bean and J. R. Johnson, J. Am. Chem. Soc., 54, 4415 (1932)

(7) H. G. Kuivila and A. R. Hendrickson, ibid., 74, 5068 (1952)

boronic acid. Titration of an aliquot showed a change of 0.0504 M in peroxide concentration. At this time another aliquot (5 ml.) was removed. To this were added one ml. conc. hydrochloric acid, 10 ml. water, 0.5 g. sodium bromide and 0.5 ml. of 0.5 M ammonium molybdate. The bromine thus formed could brominate the phenol present. After 15 min. potassium iodide was added and the iodine titrated with thiosulfate. The difference between this last titer and the preceding one indicated a change of 0.146 M in bromine concentration as compared with 0.150 M required on the basis of boronic acid originally present.

A similar determination on a reaction in 4.12 M perchloric acid showed consumption by the phenol produced in the reaction of 0.0742 M bromine vs. 0.0750 M calculated.

This procedure for quantitative estimation of phenol is a modification of that given by Siggia[8].

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(8) "Quantitative Organic Analysis via Functional Groups", S. Siggia, John Wiley & Sons, Inc., New York, 1949, p. 111

Rate Measurements A flask containing appropriate concentrations of boronic acid, buffer and sodium perchlorate was placed in a bath at 25.10 ± 0.02°. After at least 15 minutes an aliquot of hydrogen peroxide solution at the same temperature was added. Aliquots were removed at intervals and transferred to flasks containing 5 ml. 4 M sulfuric acid, 5 ml. 5% potassium iodide solution and 5 drops 0.5 M ammonium molybdate.[9]

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(9) I. M. Kolthoff and N. H. Furman, "Volumetric Analysis", Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1929, p. 392

The resulting iodine was titrated with freshly standardized sodium thiosulfate. When runs were made in acid solutions the sulfuric acid was omitted from the quenching solution. When the strongest acid solutions were used it was necessary to add ice to the quenching solution and to dilute it to at least 80 ml. before titration. This is due to the fact that the reaction between thiosulfate and the starch-iodine complex seems to be slower in strong acid which leads to danger of overtitration.

In the presence of chelating agents the catalytic effect of molybdate on the iodine-peroxide reaction is negligible and therefore the iodometric analysis is rendered unreliable. The colorimetric method involving titanium IV[10] was used.

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(10) G. M. Eisenberg, Ind. Eng. Chem., Anal. Ed. 15, 327 (1943)

Measurements were made with a Coleman junior spectrophotometer. At the wavelength of maximum absorption found (420 mμ) Beer's law is not obeyed and so a calibration curve was prepared. The optical density was not affected by any of the solutes. Some fading in the color occurred with time when boronic acid was present, but readings were always completed within two minutes so that the error introduced was never more than 0.5% in the peroxide concentration.

Determinations of pH were made with a Beckman Model H 2 pH meter.

RESULTS

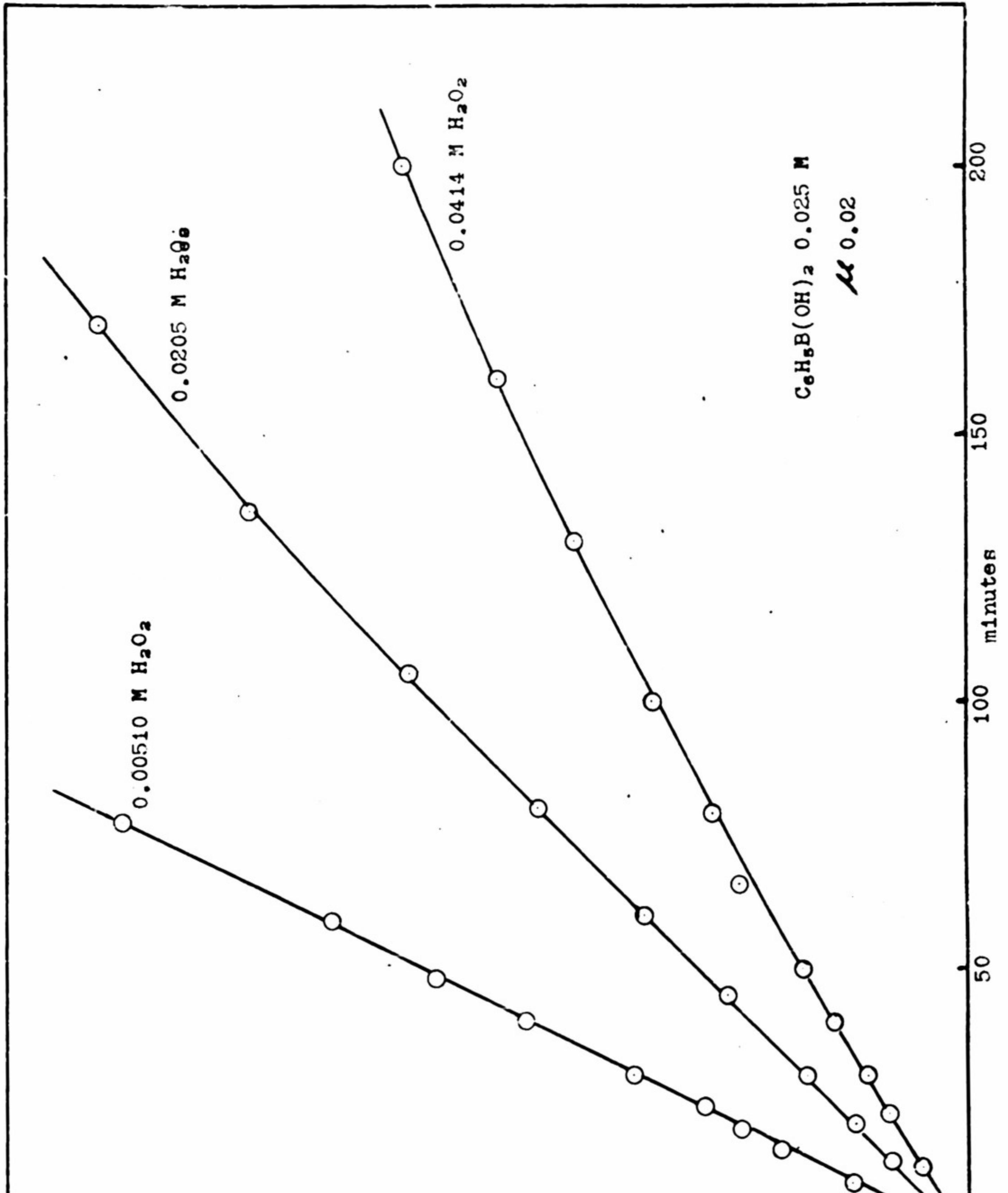
Preliminary experiments showed that the reaction proceeds at a conveniently measurable rate at 25° in water. In the absence of other substances the kinetics are complex. This is shown in Fig. 1 which represents the conventional second order plot for three reactions in which the hydrogen peroxide concentration was varied. The increase in slope with decreasing concentration indicates an order of less than one for peroxide and suggests that dissociation is involved. That this is an acid-base dissociation is shown in Fig. 2. Here it is seen that the initial slopes for the two different peroxide concentrations are the same in a buffered solution. Added phenol, acetanilide or boric acid in 0.02 M concentration did not alter the rate.

The decrease in the apparent second order rate constant observed in Fig. 2 is evidently due to the presence of a reaction second order in boronic acid. At the higher peroxide concentration a sufficiently large change in boronic acid concentration occurs to be easily manifested in the rate plot. To test this a series of runs with different initial boronic acid concentrations was made. The apparent initial second order rate constants proved to be linear functions of boronic acid concentration. Several such plots at different values of the pH are shown in Fig. 3. The observed rate constants can thus be represented by equation 1.

$$k_{obs.} = k_1 + k_2 \left[C_6H_5B(OH)_2\right] \qquad (1)$$

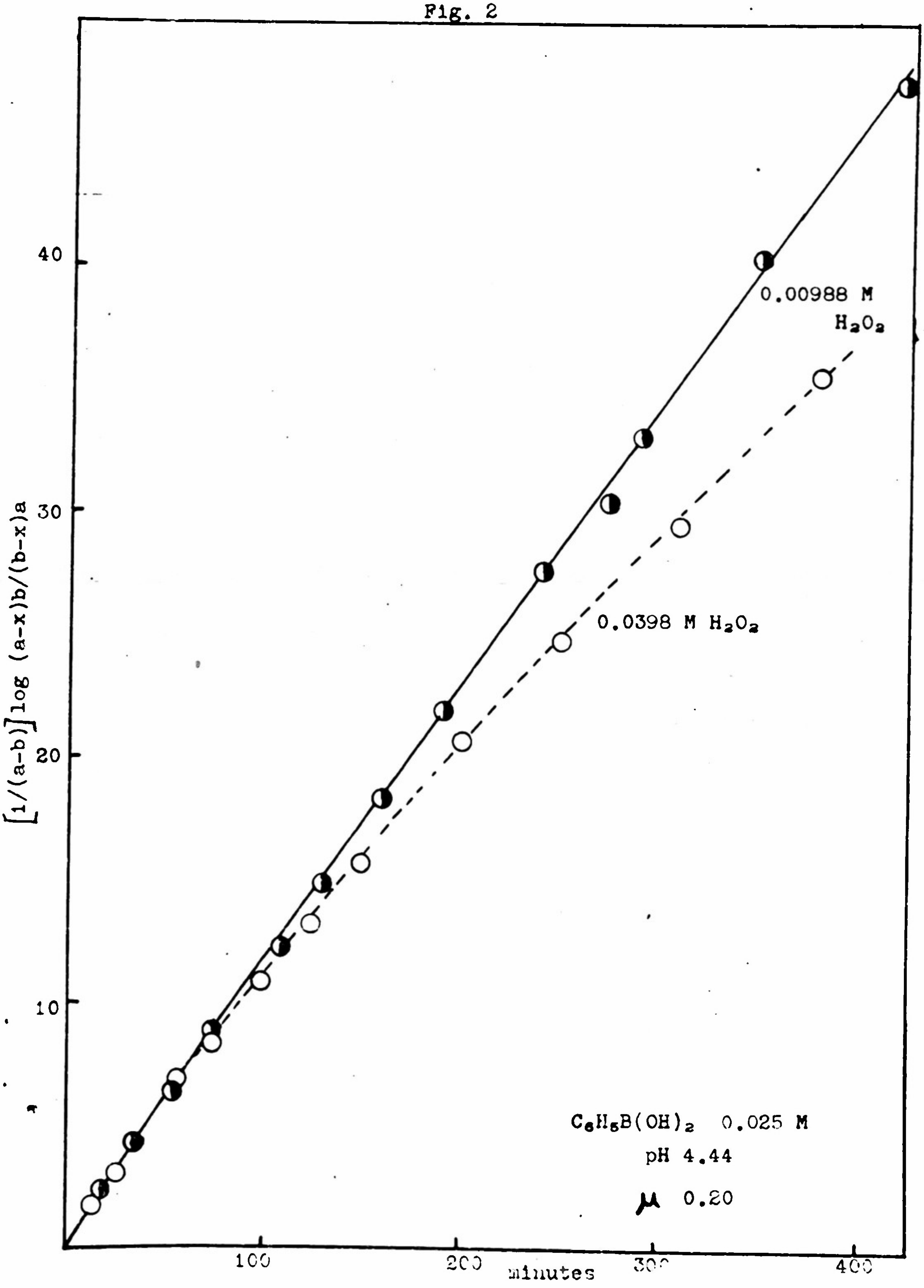
Logarithms of the values of k_1 and k_2 evaluated by the method of least squares are plotted as a function of pH in Fig. 4.

Fig. 1



0.00510 M H_2O_2
0.0205 M H_2O_2
0.0414 M H_2O_2
$C_6H_5B(OH)_2$ 0.025 M
μ 0.02
minutes
50
100
150
200
10
20
30
40
50
$[1/(a-b)] \log(a-x+b)/(b-x)a$

Fig. 2



40
30
20
10
[1/(a-b)] log (a-x)b/(b-x)a
100
200
300
400
minutes
0.00988 M H_2O_2
0.0398 M H_2O_2
$C_6H_5B(OH)_2$ 0.025 M
pH 4.44
μ 0.20

Fig. 3

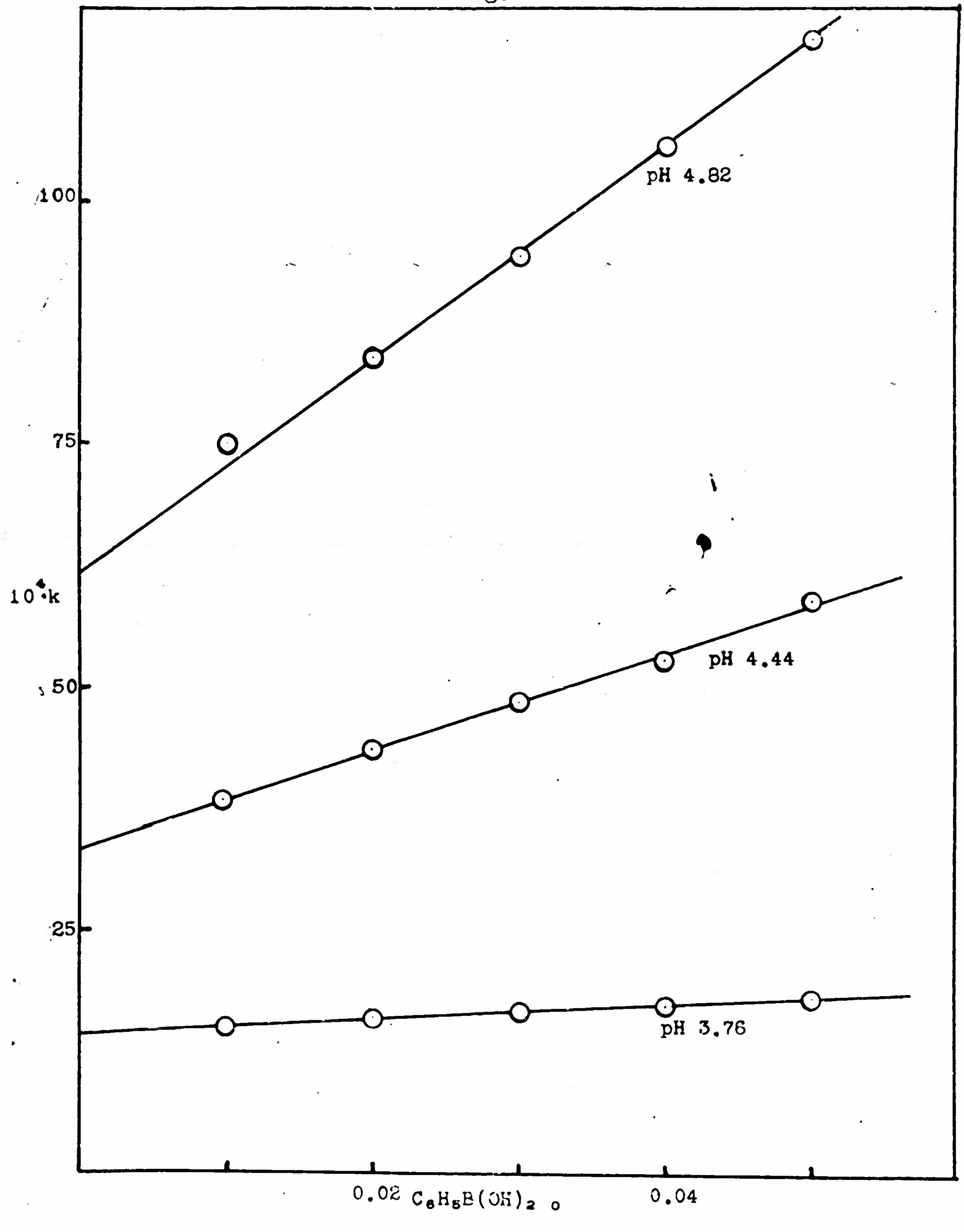
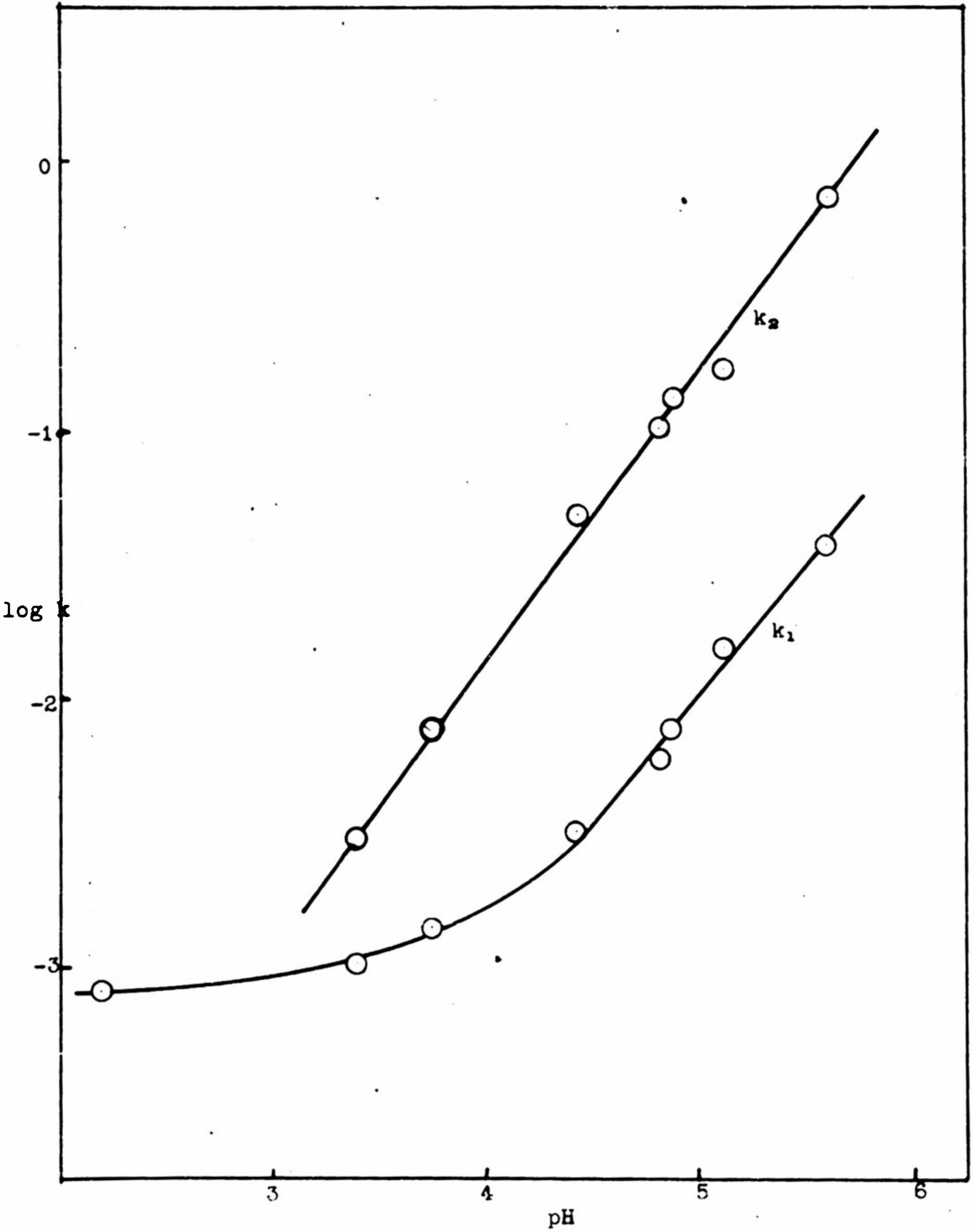


Fig. 4



The least squares slope of the k_2 plot is 1.10 in fair agreement with the theoretical value of unity for base catalysis. The terminal slope of the k_1 plot as drawn is unity.

The figures in Table 1 show that the rate is independent of buffer concentration. Thus each reaction has the characteristics of first order specific lyate ion[11] catalysis. This is confirmed by the data in Table 2 involving acetate and chloroacetate respectively as buffers. In this table, $k_{calc.}$ was computed for the boronic acid concentration given from values of k_1 and k_2 taken from Fig. 4.

Table 1.

Values of k_1 and k_2 at Different Buffer Concentrations.

Phthalate Buffer at pH 4.44

Buffer Conc. moles/l.	$10^3 k_1$ l.mol^{-1} sec.$^{-1}$	$10^3 k_2$ l.^{2} mol.$^{-2}$ sec.$^{-1}$
0.02	3.32	50.6
0.05	3.01	51.3
0.10	3.38	47.0

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(11) N. Bjerrum, Chem. Rev., 16, 287 (1935)

Table 2.

Values of $k_{obs.}$ for Various Buffers

Buffer	Buffer Concn. moles/l.	pH	$[C_6H_5B(OH)_2]_0$ moles/l x 10^3	$10^3 k_{obs.}$	$10^3 k_{calc.}$
acetate	0.05	4.88	20.0	9.92	9.9
	.05	4.88	40.0	12.6	12.4
	.05	5.24	10.0	19.8	20.2
	.05	5.24	20.0	22.8	23.4
chloroacetate	.22	3.75	40.0	1.73	1.66
	.22	3.75	20.0	1.58	1.51
	.055	3.67	40.0	1.61	1.54
	.055	3.67	20.0	1.45	1.42
citrate	.05	4.25	40.0	12.2	3.42
tartrate	.05	4.00	20.0	13.4	2.00
	.05	4.00	40.0	18.6	2.28

Tartrate and citrate, on the other hand, function as rather efficient specific catalysts. This is undoubtedly the result of their ability to function as chelating agents.

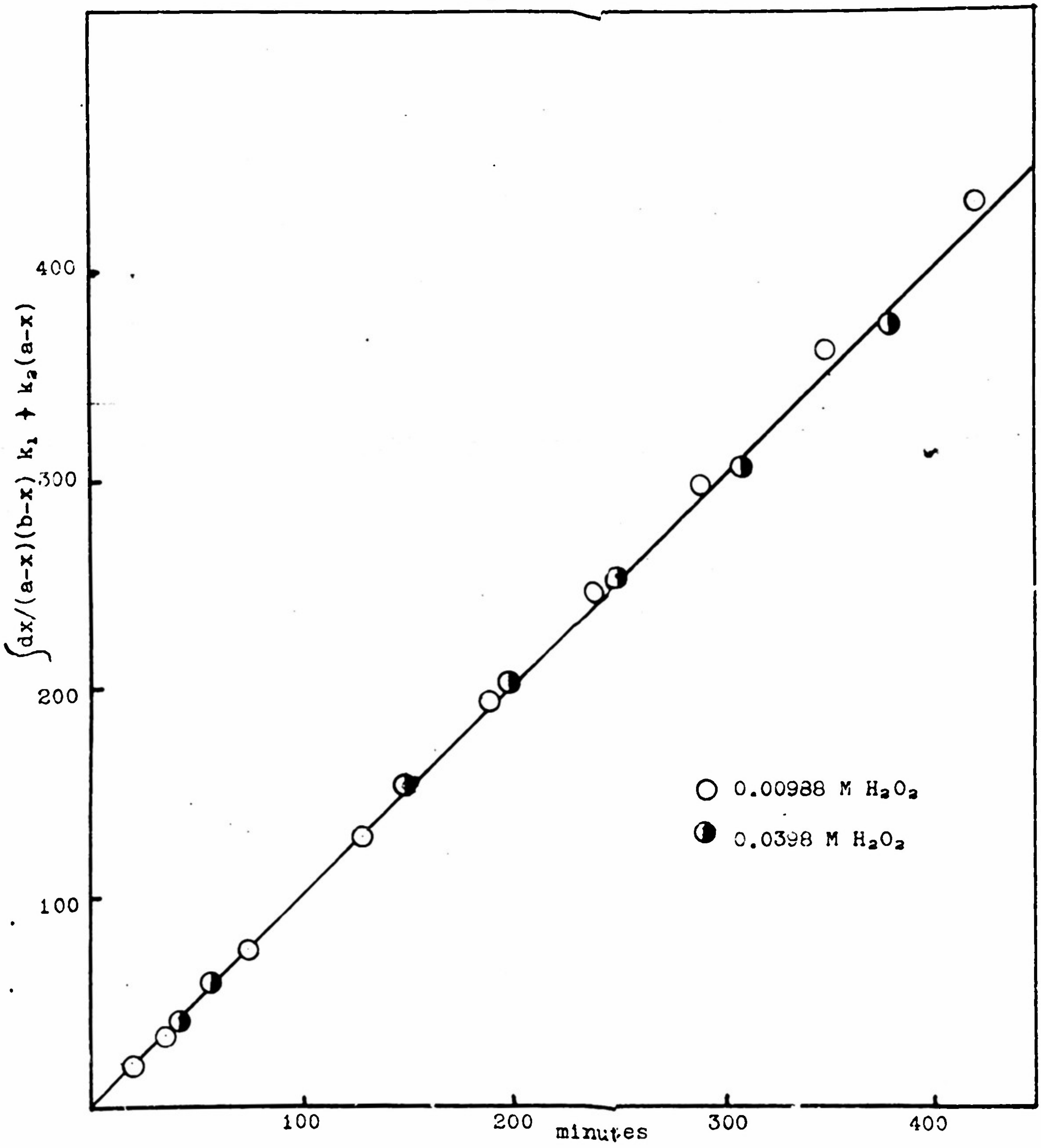
A test of the validity of equation (1) for the runs in Fig. 2 is shown in Fig. 5. The left side of the equation,

$$\frac{dx}{(a-x)(b-x)\left[k_1+k_2(a-x)\right]} = dt \qquad (2)$$

where a and b are initial concentrations of boronic acid and hydrogen peroxide respectively and x represents the concentration of the products, was evaluated by graphical integration. Values of k_1 and k_2 from Fig. 4 were used. Values of the integral agree with the time in all cases within 3% over 90% consumption of the reactant in lowest initial concentration.

The fact that the slope of the log k_1 - pH plot decreases to practically zero at pH 2 led to an investigation of

Fig. 5



∫dx/(a-x)(b-x) k₁ + k₂(a-x)
400
300
200
100
100
200
minutes
300
400
○ 0.00988 M H₂O₂
◑ 0.0398 M H₂O₂

moderately strong acid solutions of perchloric and sulfuric acids as reaction media. Under these conditions only one reaction, first order in each reactant, is observed. Second order rate constants and acid concentrations are listed in Table 3.

Table 3.

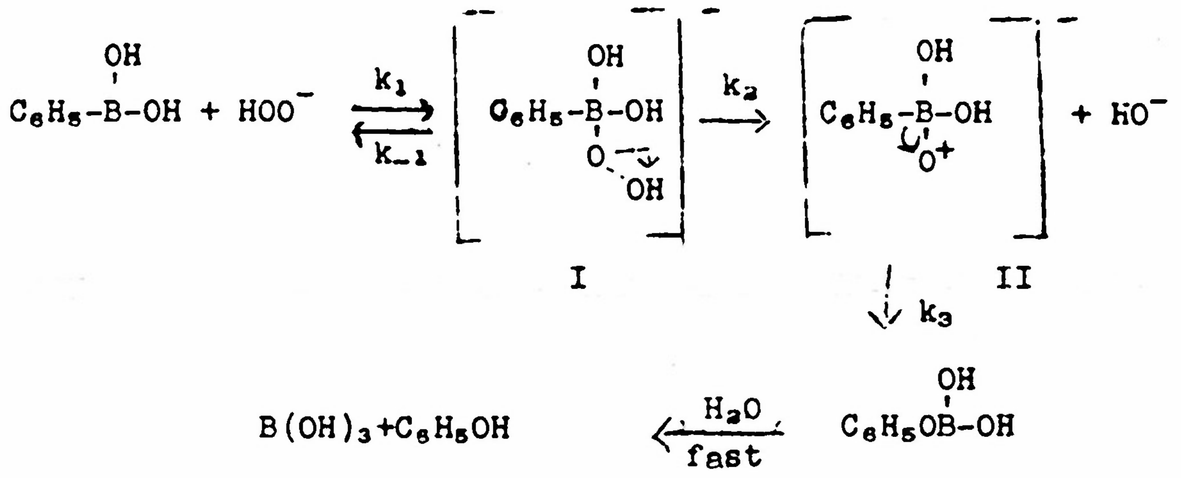
Rate Constants in Acid Solutions

Sulfuric Acid		Perchloric Acid	
moles/l	10^3k l. mol^{-1} sec^{-1}	moles/l	10^3k l. mol^{-1} sec^{-1}
1.13	9.89	.75	3.94
2.26	31.7	2.47	16.0
3.64	91.9	3.73	31.9
6.36	591.	4.12	44.0
8.99	3600.	5.93	137.
		8.15	604.

It is clear that the rate constant is not a simple function of the acid strength and that sulfuric acid is the more efficient catalyst in terms of molar concentration.

DISCUSSION

The Base Catalysis The specific lyate ion catalysis means that the rate is proportional to some species whose concentration depends only on pH. From the results represented in Figs. 1 and 2 it is clear that this species must be the hydroperoxide ion. On the basis of this fact the following mechanism for the reaction seems most reasonable.

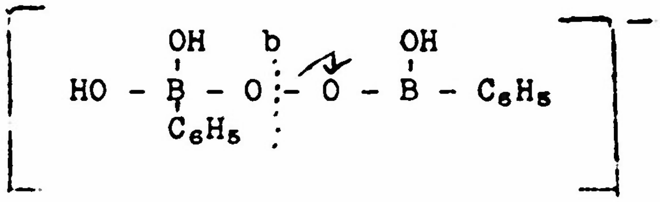


The data presented do not permit definite assignment of relative values to the rate constants. However, on the basis of the fact that esters of boronic acids appear to form and hydrolyze rapidly it may be assumed that k_1 and k_{-1} are large compared with k_2. Steps 2 and 3 may be entirely distinct as one possible extreme or simultaneous as another.

This mechanism is analagous to those generally written for the reactions of Caro's acid and percarboxylic acids with ketones to produce esters[12]. The epoxidation of α, β-

unsaturated ketones involves attack by hydroperoxid ion on the β carbon followed by loss of hydroxide ion and formation of the oxide.[13] This reaction does not occur with simple olefins in which polarization of the double bond by the carbonyl group is absent.

The intermediate in the third order reaction must be derived from two molecules of boronic acid and a hydroperoxide ion. An intermediate such as III may be reasonable. Cleavage at b would result in II and benzeneboronate anion. Thus the function of the second molecule of acid is to promote the ionic cleavage of the peroxide bond.



$$\left[HO - \underset{C_6H_5}{\overset{OH}{B}} - O \overset{b}{\vdots} - O - \overset{OH}{B} - C_6H_5 \right]^-$$

III

The Catalysis by Chelating Agents It is well known that certain polyhydroxy compounds increase the acidity of solutions of boric acid[14] and boronic acids[15]. This is attributed, in

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(12) A. Robertson and W. A. Waters, J. Chem. Soc. 1574 (1948); R. Criegee, Ann. *560*, 127 (1948); S. L. Friess, J. Am. Chem. Soc. *71*, 2571 (1949)

(13) C. A. Bunton and G. J. Minton, J. Chem. Soc., 665 (1949)

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(14) J. Boeseken, N. Vermaas and A. Th. Küchlin, Rec. trav. chim., 49, 711 (1930)

(15) G. E. K. Branch, D. L. Yabroff and B. Bettman, J. Am. Chem. Soc. 56, 1865 (1934)

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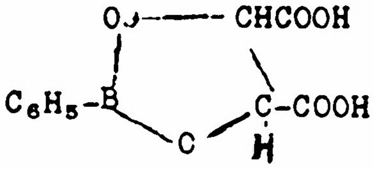
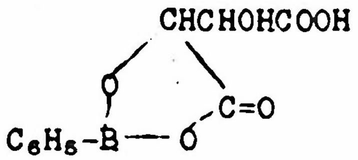
the case of boric acid, to the formation of quadricovalent chelate complexes involving one or two molecules of chelating agent. In the case of boronic acids only single chelation is possible because of the organic group attached to the boron. Formation of an intermediate, such as IV or V with tartaric acid, leads to a decrease in the O-B-O bond angle from 120° to



IV



V

one approaching the 108° of a regular pentagon. This provides a driving force for the addition of hydroperoxide ion leading to an intermediate analogous to I with tetrahedral boron. Thus the concentration of this type of intermediate would be increased, resulting in a greater rate of reaction if the rate of the subsequent slow step is comparable to that involving I.

The Acid Catalysis The decrease in slope of the k_1 plot (Fig. 4) below pH 5, along with the increase in rate in acid solutions is suggestive of acid-base catalysis. However, the rate in acid solution does not depend on either of the acidity functions Ho[16] or Jo[17]. Thus simple displacement by the conjugate acid of hydrogen peroxide and by the hydroxyl cation are ruled out as mechanistic possiblities. Various combinations of Ho and the activities of water and acid which have been tested fail to correlate the rates in the acid media. The function H_- could not be tested because values for it are not available.

Rates of Reaction of Substituted Benzeneboronic Acids with Hydrogen Peroxide The Hammett equation is $\log (k/k_0) = \rho\sigma$ where k and k_0 are rate or equilibrium constants for substituted and unsubstituted benzene derivatives, ρ is a constant characteristic of the reaction and σ is a constant characteristic of the substituent[18]. This equation correlates the rates or equilibria of a large number of reactions in the side chains of meta and para substituted benzene derivatives.

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(16) L. P. Hammett, "Physical Organic Chemistry," McGraw Hill Book Co., New York, N. Y., 1940, p. 267

(17) V. Gold and B. W. V. Hawes, J. Chem. Soc., 1951, 2102

(18) Ref. 16 ch. 7.

Some reactions involving side chains[19], electrophilic displacement in the ring[7] and molecular rearrangements with the aryl group migrating[20] are not well correlated by the equation. Absence of a correlation is generally attributed to resonance stabilization of the transition state due to conjugation between the substituent and the site of reaction[19]. Thus some conclusions concerning the nature of the rate determining step can be drawn from data on the effect of substituents.

In this investigation the rates of reaction of thirteen meta and para substituted benzeneboronic acids with hydrogen peroxide have been studied. The objectives were to test the applicability of the Hammett equation and to compare the results with those obtained in the brominolysis of benzeneboronic acids.

All reactions were carried out at 25.10 ± 0.02° in a solvent containing 25 ml. methanol per 100 ml. solution. The solvent in all cases was 0.997 M in perchloric acid. Two runs were made with each compound. The concentration of boronic acid differed by a factor of two in these runs and was in each case smaller than the peroxide concentration. Good second order kinetics were observed throughout the period of

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(19) C. G. Swain and W. P. Langsdorf, Jr., J. Am. Chem. Soc., 73, 2813 (1951)

(20) (a) W. E. McEwen and N. B. Mehta, ibid. 74, 526 (1952);
(b) S. N. Ege and K. W. Sherk, ibid. 75, 354 (1953)

observation which covered 90% consumption of boronic acid in at least one of the runs.

Rate constants are summarized in Table 4 and the logarithms are plotted versus sigma in Fig. 6. The points fall fairly close to a straight line whone slope corresponds to ρ = -0.90. However, close scrutiny of the plot indicates that the data could be better represented by a curve which is slightly concave upward.

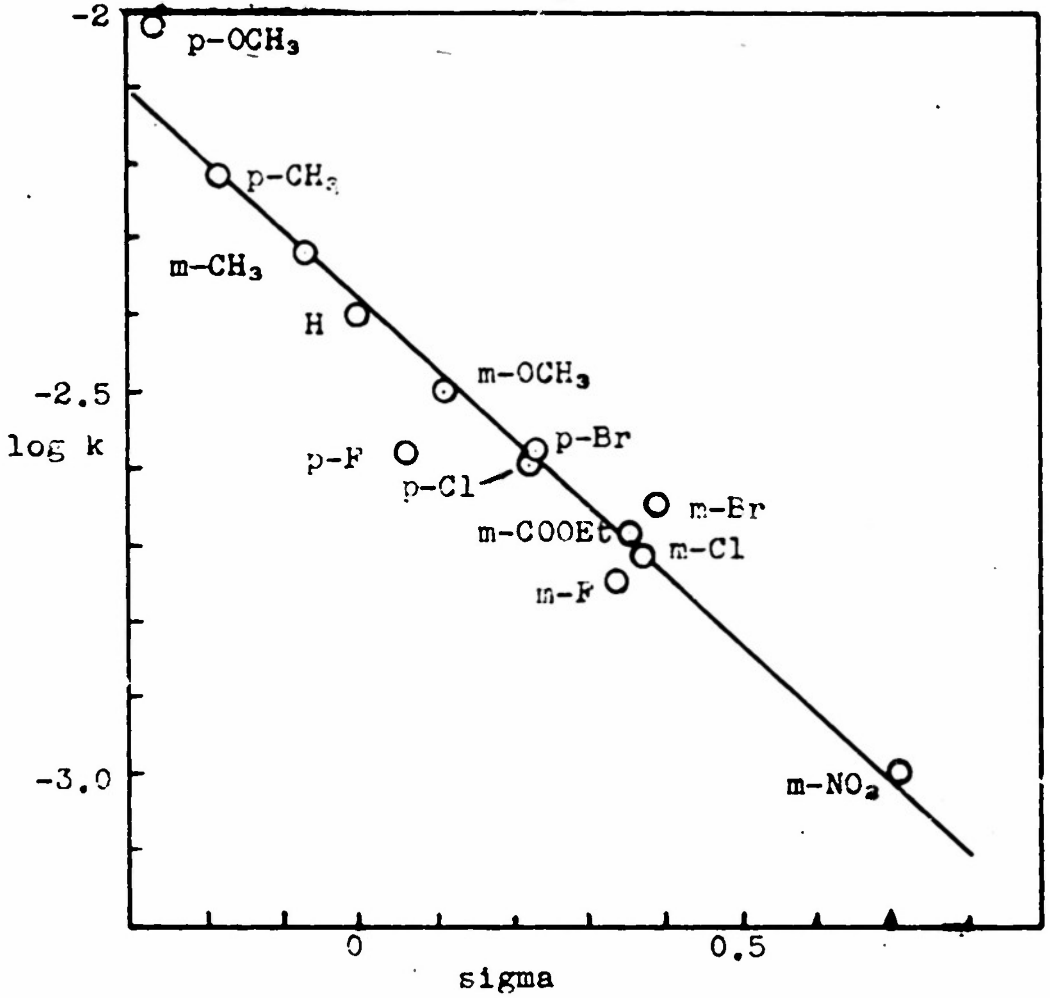
Table 4.

Rates of Reaction of Substituted Benzeneboronic Acids with Hydrogen Peroxide

	neutral eq.[a]		$k \times 10^3$		
substituent	calc.	obs.	$l\ mol^{-1}\ sec^{-1}$	log k	σ
H	103.9	104.8	3.99	-2.399	0
$p\text{-}OCH_3$	152.0[b]	155.1[c]	9.65	-2.016	-.268
$p\text{-}CH_3$	118.0	119.1	6.12	-2.213	-.170
$m\text{-}CH_3$	118.0	119.3	4.81	-2.317	-.069
p-Br	199.5[b]	200.8	2.64	-2.578	+.232
p-Cl	138.4	139.5	2.53	-2.598	+.227
p-F	121.9	122.7	2.66	-2.576	+.062
· · ·	· · ·	· · ·	· · ·	· · ·	· · ·
$m\text{-}OCH_3$	134.0	134.4	3.22	-2.492	+.115
m-Br	182.8	182.8	2.26	-2.644	+.391
m-Cl	138.4	138.0	1.95	-2.711	+.373
m-F	121.9	121.8	1.81	-2.744	+.337
m-COOEt	193.9[b]	195.9	2.08	-2.644	+.391
$m\text{-}NO_2$	148.9	149.8	1.02	-2.994	+.710

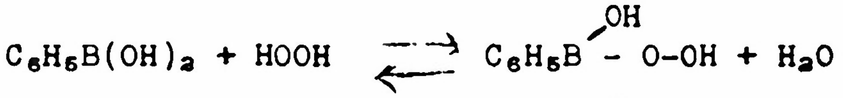
a. For anhydride except where specified
b. For acid
c. See Experimental, Section III

Fig. 6


-2
-2.5
-3.0
log k
0
0.5
sigma
p-OCH$_3$
p-CH$_3$
m-CH$_3$
H
m-OCH$_3$
p-Br
p-F
p-Cl
m-Br
m-COOEt
m-Cl
m-F
m-NO$_2$

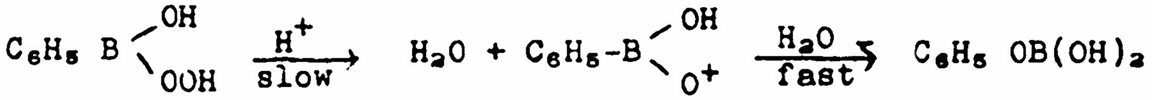
This plot is very similar to those obtained by McEwen and Mehta[20a] for the reactions of benzoic acids and diarylethylenes with hydrazoic acid, which gave rho values of -1.97 and -2.11 respectively. On the other hand the plot is quite different from that obtained in the reaction of bromine with benzeneboronic acid in aqueous acetic acid solution[7], where a clearly non-linear plot is found.

With regard to mechanism these data indicate that migration of the aryl group is not an important part of the rate determining step. Let us assume that peroxide and boronic acid react reversibly to form I or, more probably, VI in acid



$$C_6H_5B(OH)_2 + HOOH \rightleftharpoons C_6H_5B\overset{OH}{\diagup} - O{-}OH + H_2O$$

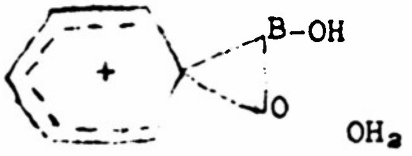
VI



$$C_6H_5\,B\begin{matrix}OH\\OOH\end{matrix} \xrightarrow[slow]{H^+} H_2O + C_6H_5{-}B\begin{matrix}OH\\O^+\end{matrix} \xrightarrow[fast]{H_2O} C_6H_5\,OB(OH)_2$$

VII

solution. The rate of reaction will be controlled by the concentration of VI (or I) and promoted by electron-releasing substituents in the benzene ring. The departure of water or hydroxide is not assisted in important degree by migration of the aryl group, so that the transition state has little contribution from structures like VIII.



VIII

II. KINETICS OF THE REACTION BETWEEN p-METHOXYBENZENEBORONIC ACID AND IODINE

An investigation of the kinetics and mechanism of the reaction of iodine with aromatic boronic acids to parallel the investigations with bromine described in the previous section has been initiated. The reaction of iodine with phenol and aniline has been carefully examined by Soper[1] and Berliner[2] and their co-workers. The iodinating species in each case is either the iodine cation or the conjugate acid of hypoiodous acid; the substrates are predominantly phenoxide ion and free aniline. It would be of interest to ascertain whether the same iodinating species are the effective ones and what other characteristics the reaction assumes when the boronic acid group is replaced instead of hydrogen.

EXPERIMENTAL

p-Methoxybenzeneboronic Acid. The acid was prepared by the method of Bean and Johnson[3]. However, considerable difficulty was encountered in its purification. Repeated crystallization from water, aqueous methanol and benzene failed to give a pure

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(1) B. S. Painter and F. G. Soper, J. Chem. Soc. 2757 (1927); F. G. Soper and G. F. Smith, ibid., 342 (1947)

(2) E. Berliner, J. Am. Chem. Soc., 72, 4003 (1950); ibid., 73, 4307 (1951)

(3) F. R. Bean and J. R. Johnson, ibid., 54, 4415 (1932)

product. The purity was tested by three methods: (a) Titration with sodium hydroxide after addition of mannitol. (b) Reaction to completion with excess iodine. (c) Reaction to completion with excess hydrogen peroxide. Molecular weights computed from consumption of these reagents were: (a) 154.5, 154.5; (b) 155, 156; (c) 155.0, 155.1; calculated, 152.0. Since these three methods of assay gave the same molecular weights it is evident that the impurity does not react with iodine. The value 155.05 was used in calculating concentrations.

All other reagents were of the purest grade available commercially and were used without further purification.

Kinetic Procedure. Stock solutions of sodium perchlorate (for adjusting ionic strength), buffer and iodine in sodium iodide solution with a ratio of iodide to iodine of 50 to 1 were prepared. A sample of boronic was placed in the reaction flask. Ten ml. methanol was added to dissolve the acid and then appropriate volumes of water, perchlorate and buffer solutions by pipet or buret. After at least thirty minutes in a bath at 25.1 ± 0.02° iodide solution at the same temperature was added at zero time. The final volume was 200 ml. Aliquots were removed periodically, quenched by transfer into a flask containing 10 ml. 2 N sulfuric acid and then titrated with 0.01 N thiosulfate. The zero titer was determined by titration of an aliquot from a solution made up in the same way as the reaction mixture with the exception that the boronic acid was omitted.

Kinetic data for two typical runs are listed in Table 1. Rate constants were computed by the usual second order integrated rate equation $[1/(a-b)] \log (a-x)b/(b-x)a = kt$.

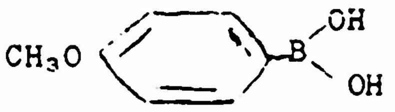
Table 1.

Run K-5: 0.004394M $CH_3OC_6H_4B(OH)_2$

0.003077M I_2, 0.150M NaI, 0.500M NaOAc, 0.056M HOAc.

pH = 5.58 $\mu = 0.741$

Time in Minutes	$(b-x) \times 10^3$	k $l.\ mol^{-1}\ min.^{-1}$
0	3.077	-
2	2.460	24.5
4	2.012	24.6
6	1.690	24.4
8	1.439	24.2
10	1.240	24.1
13	0.996	24.3
16	0.825	24.0
19	0.689	23.9
24	0.515	24.0
30	0.375	23.9
37	0.265	23.8

Run # L-1: 0.016160M  ,

$0.003085M\ I_2$, 0.150M NaI, 0.100M NaOAc, 0.900M HOAc.

pH = 3.59 $\mu = 0.742$

Time in Minutes	$(b-x) \times 10^3$	k l. mol^{-1} min.$^{-1}$
0	3.085	-
10	2.923	0.291
35	2.575	0.325
62	2.258	0.320
92	1.951	0.321
123	1.687	0.319
151	1.484	0.318
180	1.294	0.319
232	1.032	0.316
272	0.867	0.315
378	0.552	0.314
469	0.380	0.312
532	0.294	0.311

RESULTS

Kinetic Order. When ionic strength, buffer and iodide concentrations and pH are maintained constant the reaction is first order in boronic acid and in iodine. This is shown by the data in Table 2.

Table 2.

Variation of Initial Concentrations of Iodine and Boronic Acid

pH, 4.42; μ, 0.743; NaOAc, 0.240M; HOAc, 0.361M

initial boronic acid molarity x 10^3	initial iodine molarity x 10^3	sodium iodide molarity	k l. mol^{-1} min^{-1}
1.989	4.01	0.200	1.50
4.025	4.02	.200	1.50
5.927	4.01	.200	1.48
8.039	4.02	.200	1.48
9.827	4.01	.200	1.49
9.862	2.00	.500	0.546
9.860	4.04	.500	0.550
9.862	8.06	.500	0.539
9.866	16.16	.500	0.554

Effect of Iodide Concentration Variation of the iodide concentration is helpful in determining which of the several possible iodinating agents may be effective in the reaction. The results obtained when the iodide concentration was varied over a five-fold range are listed in Table 3. In each run

Table 3.

Effect of Iodide Ion Concentration on Rate

NaOAc, 0.240M; HOAc, 0.36M ; μ, 0.743; pH, 4.41

initial iodine molarity x 10^3	sodium iodide molarity	k l. mol^{-1} $min.^{-1}$	k x iodine conc.
2.01	0.0999	2.99	0.299
3.05	.1524	1.92	.293
4.01	.200	1.49	.298
7.08	.350	0.826	.289
8.12	.400	0.729	.292
10.03	.499	0.573	.286

the ratio of iodide to iodine (both stoichiometric) was the same. The constancy of the product of iodide concentration and rate constant reveals that the rate is inversely proportional to the first power of iodide concentration.

Effects of pH and Buffer Concentration. Kinetic runs have been made at four pH's using acetate buffers. At least five runs with varying total buffer concentration were made at each pH. Results are plotted in Figs. 1 and 2. Extrapolation to zero buffer concentration gave rate constants which are plotted in Fig. 3.

Two noteworthy characteristics evolve from the data. First, the rate constants decrease with increasing buffer concentration. The effect becomes more pronounced as the pH decreases. The curvature in the plot at pH, 3.59, can be attributed to a medium effect because at the highest acetate concentration the acetic acid concentration is 4.5 M. Secondly, the plot in Fig. 3 is linear with unit slope, at least above pH 4.5. Thus the rate is proportional to the reciprocal of the first power of hydrogen ion concentration.

DISCUSSION

From the foregoing results the following expression can be used to represent the rate of reaction of iodine and p-methoxybenzeneboronic acid.

Fig. 1

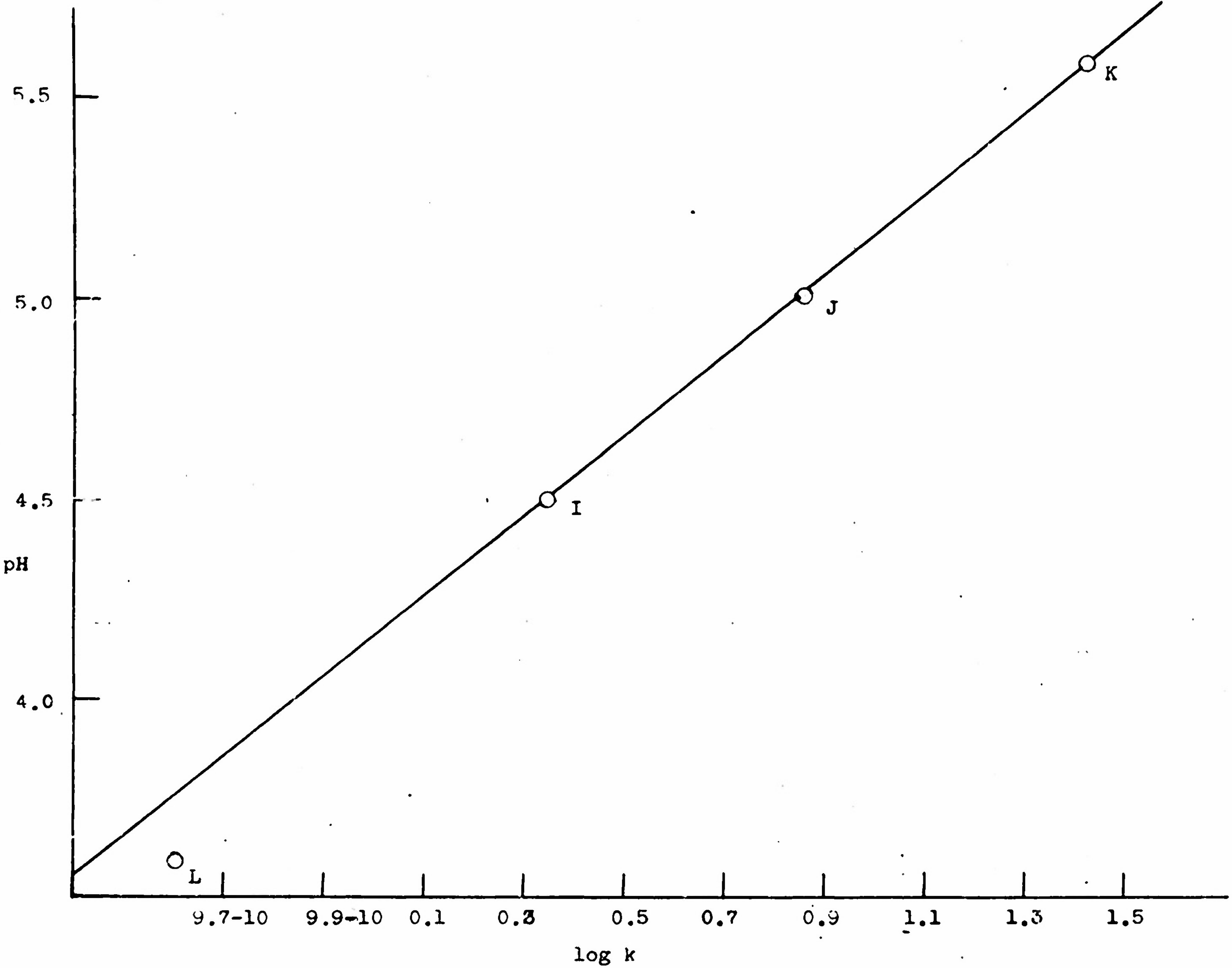
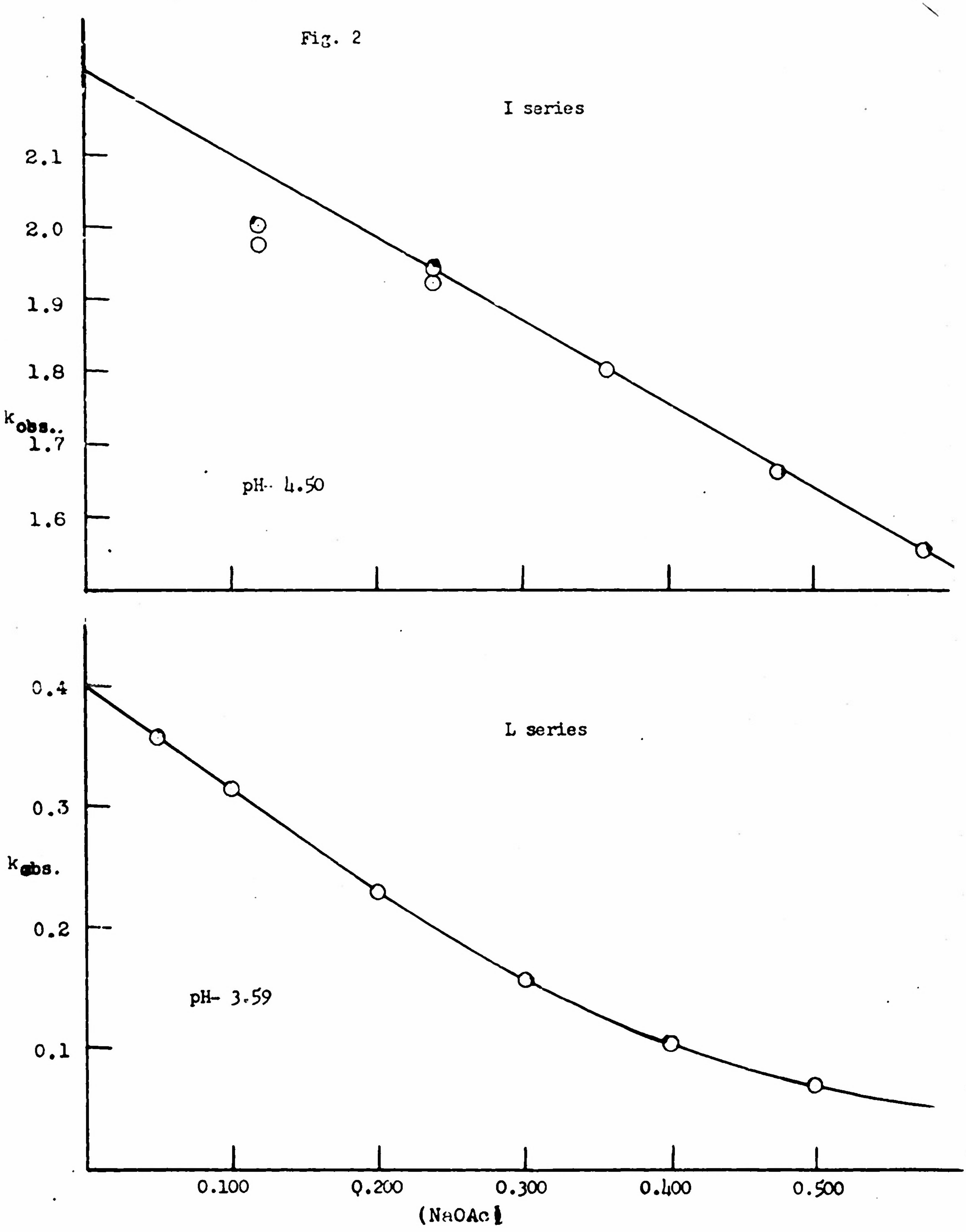


Fig. 2



I series
2.1
2.0
1.9
1.8
kobs.
1.7
pH- 4.50
1.6
L series
0.4
0.3
kobs.
0.2
pH- 3.59
0.1
0.100
0.200
0.300
0.400
0.500
(NaOAc)

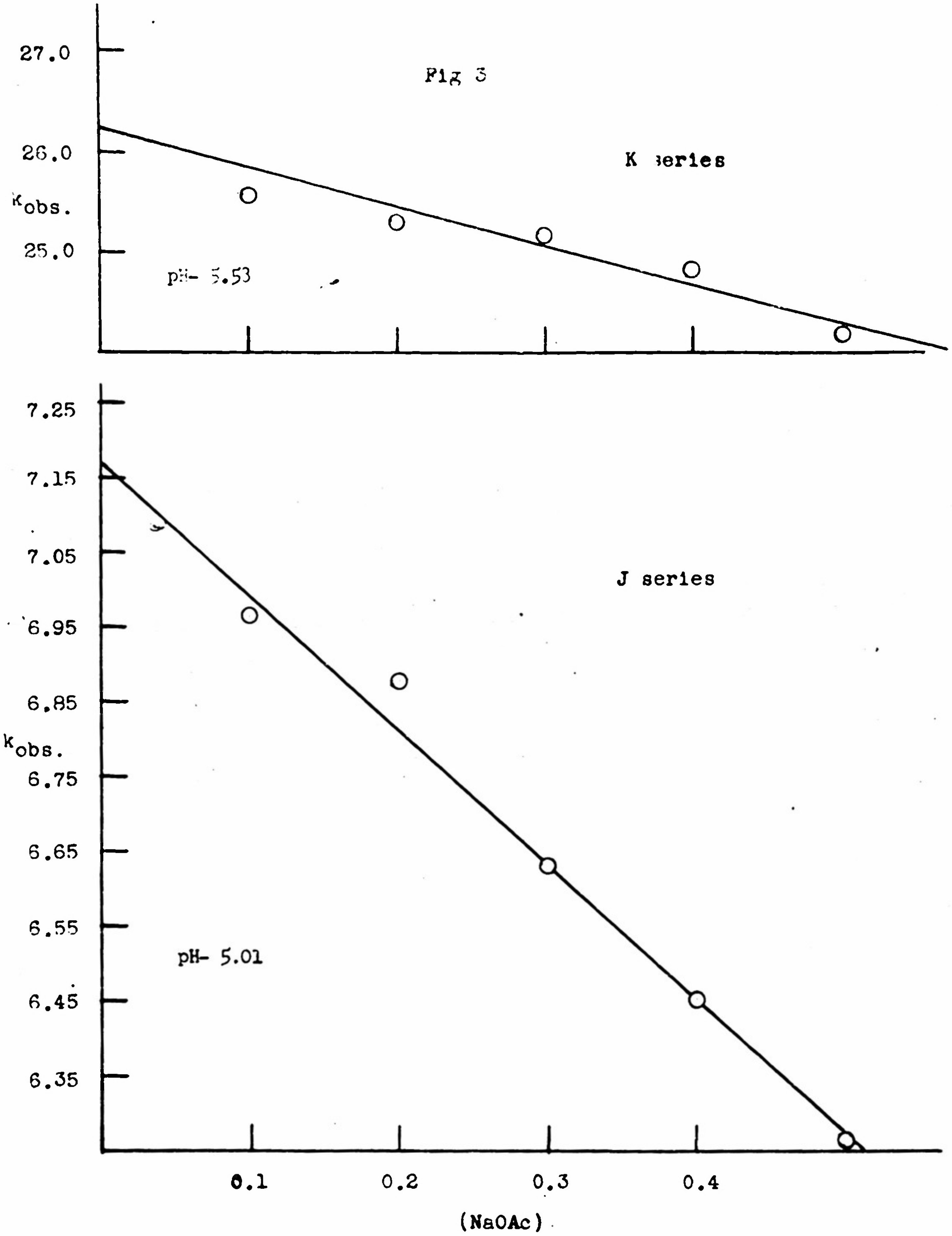


Fig 3

27.0
26.0
$k_{obs.}$
25.0
pH- 5.53
K series
7.25
7.15
7.05
6.95
6.85
$k_{obs.}$
6.75
6.65
6.55
6.45
6.35
J series
pH- 5.01
0.1
0.2
0.3
0.4
(NaOAc)

(1) $$\frac{dx}{dt} = \frac{k_{obs.}\ [RB(OH)_2]\ [I_2]}{[H^+]\ [I^-]}$$

Of the several species derived from iodine present in aqueous iodide solution only I_2, I^+, H_2OI^+ and HOI are likely to function as effective iodinating agents. The concentration of iodine alone among these depends on the reciprocal of the iodide concentration. Therefore it must be the iodinating agent.

Dependence upon the reciprocal of the hydrogen ion concentration immediately suggests that the conjugate base of the boronic acid is the substrate. Given the equilibria (2) and (3) we can rewrite equation (1) as follows.

(2) $$I_2 + I^- \rightleftharpoons I_3^- \qquad K_I$$

(3) (a) $$RB(OH)_2 \rightleftharpoons RBO_2H^- + H^+ \qquad K_{HA}$$

or (b) $$RB(OH)_2 + H_2O \rightleftharpoons RB(OH)_3^- + H^+$$

(4) $$\frac{dx}{dt} = k\ [RBO_2H^-]\ [I_2]_{free} = k\ \frac{K_{HA}}{K_I}\ \frac{[RB(OH)_2]\ [I_3^-]}{[H^+]\ [I^-]}$$

Hence, $k_{obs} = \dfrac{k\ K_{HA}}{K_I\ [H^+]\ [I^-]}$. Equation (4) contains $[I_3^-]$ instead of $[I_2]$. This is a fair approximation since, with the large excess of iodide, most of the iodine is tied up as triiodide.

The decrease in rate with buffer concentration is unusual. Scrutiny of the data reveals that molecular acetic acid is probably responsible for the effect. For acetic acid concentration of 0.367M the ratio k_0 / $k_{0.367M}$ at pH values of 5.0, 4.5 and 3.6 are 1.14, 1.15 and 1.10 respectively. It is highly improbable that the formation of acetyl hypoiodite could account for this effect. This leaves reaction with boronic acid or triiodide as alternatives. More information will be more helpful than further speculation in accounting for the effect.

III. KINETICS AND MECHANISM OF THE REACTION OF BROMINE WITH AROMATIC BORONIC ACIDS

A. Kinetic Studies with m-Chlorobenzeneboronic Acid

In a previous investigation[1] the kinetics of the reaction of benzeneboronic acid and bromine in aqueous acetic acid were investigated. The results led to the conclusion that molecular bromine attacks a quadricovalent boron intermediate in the rate determining step. Due to limitations imposed by the use of an acidic solvent it was decided to supplement this work by investigations in aqueous solution.

At first p-bromobenzeneboronic acid was used in aqueous dioxane. Numerous difficulties were encountered with this system so it was abandoned. It was decided to study m-chlorobenzeneboronic acid in pure water in which its solubility, in contrast to that of the other acid, was high enough for the purposes of the investigation.

EXPERIMENTAL

m-Chlorobenzeneboronic Acid. The acid was prepared by the method of Bean and Johnson[2], crystallized from water, dried for 2 hours at 110° and recrystallized from benzene. After repetition of this process the anhydride obtained had m.p. 181.5 - 183°; lit.[3] 178 - 179°; neutral equivalent 138.0;

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(1) H. G. Kuivila and E. K. Easterbrook, J. Am. Chem. Soc., 73, 4629 (1951)

(2) F. R. Bean and J. R. Johnson, ibid., 54, 4415 (1932)

calc. 138.4.

Other reagents were the purest available commercially and were used as obtained. Sodium perchlorate, dried at 110° to constant weight and stored in a desiccator, was used in adjusting ionic strengths.

Kinetic Procedure. The kinetic procedures was similar to that in the studies with iodine, except that the quenching solution contained 5 ml. 10% potassium iodide and 5 ml. acetic acid. The temperature was 25.00 ± 0.02°.

Second order rate constants were calculated as before. Data for a representative run are summarized in Table I.

Table 1.

Run $E^{1.5}_{008}$: pH 4.20; sodium acetate, 0.45 M; acetic acid, 1.05 M; sodium bromide, 0.25 M; boronic acid, 0.008 M; bromine, 0.00501 M; thiosulfate, 0.01293 N; 10.0 ml. aliquots

time in minutes	titer	k x 100 l. mol.$^{-1}$ sec.$^{-1}$
0	7.75	-
7	6.35	6.33
13	5.40	6.47
20	4.55	7.15
27	3.90	6.49
37	3.18	6.48
47	2.65	6.43
88	1.37	6.45
135	0.70	6.44

RESULTS

Kinetic Order. The reaction is first order in each of the reactants. This is shown by the data in Table 2 in which a

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(2) H. G. Kuivila and A. R. Hendrickson, ibid., 74, 5068 (1952)

twelve-fold variation in boronic acid and a four-fold variation in bromine concentration are represented.

Table 1.

Variation of Initial Concentrations of Boronic Acid and Bromine

pH 4.20; acetate, 0.45 M; acetic acid, 1.05 M; sodium bromide, 0.25 M; μ, 0.70; initial bromine, 0.0050 M.

boronic acid moles / l.	k x 100 l. mol.$^{-1}$ sec.$^{-1}$
0.03	6.36
.02	6.43
.01	6.45
.008	6.57
.008	6.43
.006	6.59
.004	6.66
.0025	6.73

pH, 4.15; acetate, 0.30 M; acetic acid, 0.70 M; sodium bromide, 0.25 M; μ, 0.70; boronic acid, 0.004 M.

0.002	7.51
.005	7.67
.008	7.79

Effect of Bromide Ion Concentration. The effect of variation in bromide ion concentration from 0.1 M to 0.4 M at pH 4.15 is shown in Table 3.

Table 3

Variation of Bromide Ion Concentration

acetate, 0.30 M; acetic acid, 0.70 M; μ, 0.70.

bromide moles / l.	k x 100 l. mol.$^{-1}$ sec. $^{-1}$	k x $[Br^-]$ x 100
0.10	15.2	1.52
0.25	7.63	1.91
0.40	4.89	1.96

The third column lists the products of rate constants and bromide ion concentration which is seen to be constant for the higher values of the latter. Although more data is needed the indication is that the rate depends on the reciprocal of bromide ion concentration.

Effect of Buffer Concentration. Data are available only for pH 4.15. Rate constants and corresponding buffer concentrations are listed in Table 4. It is clear that the rate constant decreases with increased buffer concentration - a characteristic observed also in the reaction involving iodine.

Table 4.

Effect of Buffer Concentration

acetate/acetic = 3/7; μ, 0.7

buffer moles / l.	k x 100 l. $mol.^{-1}$ $sec.^{-1}$
0.40	8.76
1.00	7.67
1.50	6.66

DISCUSSION

The results obtained to date indicate a very definite parallelism with those described in section II on the reaction with iodine. Kinetics are first order in stoichiometric concentrations of reactants. The inverse dependence of rate on bromide ion concentration shows that molecular bromine is the brominating agent. Furthermore, the effect of buffer concentration is very similar in each case. Here the ratio of k at zero buffer (0.0954) to that in a solution containing 0.367 M acetic acid (0.0856) is 1.11. This is within the range of values (1.15 to 1.10) observed in the other reaction.

B. Effect of Substituents

In connection with the study of the effect of substituents on the rate of reaction of benzeneboronic acid and bromine[3] several more meta and para substituted acids have been prepared. The substituents are m-OCH_3, m-Br, m-F, p-F, p-C_6H_5, and p-I. Attempts to prepare m-iodobenzeneboronic acid have failed thus far but are continuing.

Experimental. The preparation of the p-iodo acid has not been described in the literature. p-Diiodo benzene was prepared by iodination of iodobenzene[4]. This compound was converted to the monomagnesium iodide and added to butyl borate; the product was hydrolyzed to give the acid.

$$\begin{tikzcd}
p\text{-}C_6H_4I_2 + Mg \arrow[r] & p\text{-}IC_6H_4MgI \arrow[r, "B(OBu)_3"] & p\text{-}IC_6H_4B(OBu)_2 \arrow[d, "H_2O"] \\
& & p\text{-}IC_6H_4B(OH)_2
\end{tikzcd}$$

To 5.4 g. (0.22 mole) magnesium turnings and 50 ml. dry anisole was added dropwise a solution of 73.2 g. (0.22 mole) p-diiodobenzene in 175 ml. dry anisole. This solution was kept warm to prevent separation of the diiodobenzene. Ethyl iodide was added to start the reaction. As the reaction proceeded the reaction mixture became dark brown. After the

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(4) R. L. Datta and N. R. Chatterjee, J. Am. Chem. Soc., 41, 293 (1919)

diiodobenzene had all been added and evolution of heat had ceased stirring was continued for a half hour whence only a small amount of magnesium remained.

This solution was added dropwise to 75 ml. (0.28 mole) butyl borate in 175 ml. dry ether cooled in a dry ice-acetone bath. After warming to room temperature over night the reaction mixture was poured on 135 g. ice and 7 ml. conc. sulfuric acid. The resulting layers were separated and the water layer extracted with three 50-ml. portions of ether. These were combined with the original extract and extracted with four 50-ml. portions of 10% sodium hydroxide. These were combined and acidified with sulfuric acid, yielding a brown resinous material and white solid which were filtered off and extracted with portions of hot dilute sulfuric acid until a precipitate no longer appeared in the extract on cooling. The combined precipitates were tan in color, 9.8 g. Crystallization from benzene, and twice from water (treated with Norite) yielded white needles of the acid which after drying at 110° for three hours yielded the anhydride, 3.2 g., 6.3% yield, m. p. 314-318°.